

DURATION OF MOLECULES IN UPPER QUANTUM STATES

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ABSTRACT

Values of rate of decay and mean life of atoms and molecules in upper quantum states calculated from data on the intensity of absorption lines.—By combining Füchtbauer's method of determining from the intensity of absorption lines the probability that a molecule will absorb a quantum of energy, with Einstein's views as to the mechanism of light absorption and emission, the following equation is derived for calculating the rate at which molecules jump from upper to lower quantum states:

$$A_{21} = \left(\frac{8\pi\nu^3}{c^2 N_1} \right) \left(\frac{p_1}{p_2} \right) \int_0^\infty \alpha d\nu$$

where A_{21} is the chance per unit time that a molecule will jump spontaneously from quantum state 2 to quantum state 1, ν is the frequency of the light emitted in such a jump, p_1 and p_2 are the a priori probabilities of quantum states 1 and 2, and α is the absorption coefficient of the substance measured under conditions such that N_1 is the number of molecules per unit volume in the lower quantum state 1. The integral $\int \alpha d\nu$ is to be taken over the total effective width of the absorption line corresponding to the passage of molecules from quantum state 1 to quantum state 2. The mean life τ of molecules which decay from state 2 to state 1 is the reciprocal of A_{21} . Values of A_{21} and τ are calculated from existing data for the *mercury line* $\lambda 2537$, for a number of lines belonging to the *alkali doublets*, for the *iodine line* $\lambda 5461$, and for a very considerable number of lines belonging to the rotation-oscillation *spectra of the hydrogen halides*. The values obtained agree with the meager data made available by other experimental methods. From these results the following conclusions are drawn.

The mean life of molecules and atoms in upper quantum states may vary for different states at least over the range 1 to 10^{-8} seconds. The rate of decay is not a simple function of the frequency of the emitted light. The rate corresponding to the emission of a line of high frequency may be greater or less than that for a line of lower frequency. The data now available for the alkali doublets $Is - mp_1$ and $Is - mp_2$ indicate a higher rate of decay the smaller the change in total quantum number for the line under consideration. The rate of decay from a given mp_1 state is m times as great as from the corresponding mp_2 state (already stated in another form by Füchtbauer and Hofmann). In the case of the rotation-oscillation spectra of the hydrogen halides the rate of decay is greater for quantum states with one unit of oscillation and many of rotation, than for those with one unit of oscillation and only a few of rotation; and in the case of different molecules but the same quantum numbers the rate of decay is greater for the molecule with the greater frequency of oscillation.

Finally the possibility and method of calculating absolute values of A_{21} from the *Bohr correspondence principle* is indicated.

I. INTRODUCTION

THE interpretation of data on the positions of spectral lines has furnished us with relatively complete and precise information as to the energy contents of atoms and molecules in their different quantum states, and with considerable information as to the internal atomic or molecular configuration corresponding to these different states. At present, however, we have very little information as to the length of time that a molecule stays in a given quantum state, or as to the mechanism by which it jumps from one quantum state to another. Further knowledge in these directions may be of great assistance in promoting that reconstruction of theoretical physics which will be necessary for the reconciliation of wave theory and quantum theory.

In the present article we shall present a method of calculating from data on the intensity of absorption lines, the average time τ that molecules remain in an activated state before returning to their normal state by the re-emission of radiant energy. This time τ will then be calculated for a considerable number of different quantum jumps, the results will be compared with the meagre information provided by other methods of attack, and certain preliminary theoretical conclusions will be drawn.

The calculations are based on Füchtbauer's¹ method of determining from the intensity of absorption lines the probability P that a molecule will absorb a quantum of energy when illuminated with light of unit intensity. Füchtbauer's quantity P is evidently simply related to Einstein's² quantity B_{12} which is the probability that a molecule will become activated when surrounded by light of unit density, and this in turn can be shown to be related to A_{21} and B_{21} which are Einstein's probabilities, respectively, of free emission and of emission through negative absorption. The former of these A_{21} is the reciprocal of the mean life τ of the molecules in the upper quantum state.

The experimental data necessary for the calculations include a knowledge of the value of the absorption coefficient at every point across the width of the absorption line which corresponds to the quantum jump connecting the two states of the molecule in question, and the calculations possible at the present time are limited by the scarcity of such information. The work of Füchtbauer and his associates,³ however, has provided us with some excellent data for certain quantum jumps in the cases of

¹ Füchtbauer, *Phys. Zeits.* **21**, 322 (1920)

² Einstein, *Phys. Zeits.* **18**, 121 (1917)

³ Füchtbauer and Hofmann, *Ann. der Phys.*, **43**, 96 (1914);
Bartels, *Ibid*, **65**, 143 (1921);

Füchtbauer, Joos and Dinkelacker, *Ibid*, **71**, 204 (1923)

mercury, sodium, caesium and iodine, while the work of Imes⁴ gives us data for many quantum jumps for the hydrogen halides.

We may now proceed to the theoretical development, and shall need first of all to consider the factors which determine the width of a spectral line.

II. THE WIDTH OF ABSORPTION LINES

Absorption lines in gases and vapors have, as is well known, a small but finite width, the intensity of absorption falling off rapidly on both sides of an approximately central maximum. In terms of the quantum theory this distribution of intensities within the line finds its main explanation in the hypothesis that the molecules which absorb the light are not all of them in exactly the same condition, but are moving with various velocities relative to the on-coming light, and are variously affected by stray electromagnetic fields from neighboring molecules. The varying velocities of the molecules leads to a broadening of the line in accordance with the Doppler effect, and the result of the various electromagnetic fields is to affect the energy levels in the molecules and hence the magnitude of the absorbed quantum $h\nu$ and thus also lead to a broadening of the line.

The question as to what would be the width of an absorption line in case the absorbing molecules were all stationary and far enough apart to be unaffected by each others' fields is one of great theoretical interest for the quantum theory.⁵ It is a question, however, which need not now detain us, since the actual width of the absorption lines which we shall consider is almost certainly much greater than the limiting width which would be produced by stationary isolated molecules, and we can neglect this limiting width in comparison with the broadening produced as described in the preceding paragraph.

III. ABSORPTION COEFFICIENT α AND PROBABILITY OF ACTIVATION P_{12}

Let us now investigate the intensities of absorption within an absorption line. Consider a beam of light of total intensity I measured in units of energy per unit area per unit time, falling on a layer of the

⁴ Imes, *Astrophys. J.* **50**, 251 (1919)

⁵ The extreme point of view of indivisible light quanta might lead to a value of zero for the width of line absorbed by stationary isolated molecules. From a less extreme point of view the width might have a very small value of the order calculated by quasi-classical methods. (See Epstein, *Proc. Münchener Akad.*, p. 73, 1919. In any case, however, this limiting width is probably very small compared with the actual width produced with gases at moderate pressures.

absorbing medium of unit cross section and thickness dx . For the intensity of the light of a given frequency I_ν , we shall write,

$$I_\nu = dI/d\nu \quad (1)$$

Furthermore, in accordance with the discussion of the foregoing section, if N_1 is the total number of molecules per unit volume in the lower quantum state we may write

$$\delta N_1 = (\partial N_1 / \partial \nu) d\nu dx \quad (2)$$

as the number of molecules in the layer in question which are so affected by their velocity and the field from neighboring molecules that they can respond to and absorb light of frequencies lying in the spectral range ν to $\nu + d\nu$. Hence if we assume that the chance of picking up a quantum of energy $h\nu$ is directly proportional to the intensity I_ν within the range ν to $\nu + d\nu$ and to the number of molecules that can respond, we may write for the energy absorbed per second within the range ν to $\nu + d\nu$ when light is passing through the layer

$$-d(I_\nu d\nu) = P_{12} h\nu I_\nu (\partial N_1 / \partial \nu) d\nu dx \quad (3)$$

where P_{12} is the chance per unit time that a molecule will be activated under the action of light of unit intensity. Integrating with respect to x , we obtain for the intensity at any distance x

$$I_\nu = I_\nu^0 e^{-P_{12} h\nu (\partial N_1 / \partial \nu) x} \quad (4)$$

where I^0 is the intensity at $x=0$. If we write Eq. (4) in the form

$$I_\nu = I_\nu^0 e^{-ax} \quad (4')$$

where a is the absorption coefficient for the frequency in question, we can then make the identification

$$a = P_{12} h\nu (\partial N_1 / \partial \nu). \quad (5)$$

If we now integrate a over the complete width of the spectral line, assuming P_{12} constant and neglecting the slight change in ν which will be allowable owing to the narrow effective width of the line, we obtain

$$\begin{aligned} \int_0^\infty a d\nu &= P_{12} h\nu \int_0^\infty (\partial N_1 / \partial \nu) d\nu = P_{12} h\nu N_1 \\ P_{12} &= \frac{1}{N_1 h\nu} \int_0^\infty a d\nu = \frac{\lambda}{N_1 hc} \int_0^\infty a d\nu \end{aligned} \quad (6)$$

where λ is the wave-length corresponding to ν .

IV. DISCUSSION OF THE PROBABILITY OF ABSORPTION P_{12}

Except for a difference in symbolism, Eq. (6) for the probability of activation P_{12} is the same formula as that obtained by Füchtbauer,

although the method of derivation strives to attain somewhat greater clarity.⁶

In carrying out the integration, the probability P_{12} was taken as a constant independent of the frequency. This is presumably not strictly true since the molecules that absorb different frequencies are differently affected by the fields from neighboring molecules, and hence might be differently susceptible even to light of the proper frequency. Some idea of the possible effect of neighboring molecules on the value of P_{12} may be obtained from the experiments of Füchtbauer, Joos, and Dinkelacker³ which show that the total value of the integral $\int a d\nu$ for the mercury line $\lambda 2537$ decreases to about one half when nitrogen at a pressure of 50 atm. is added to the dilute mercury vapor. This indicates that neighboring molecules have only a moderate effect on P_{12} and we can safely regard the value obtained from Eq. (6) as a reasonable sort of average.

In the derivation of Eq. (6), presented in the preceding section it was tacitly assumed that all the light absorbed by the molecules in passing from the lower to the upper quantum state was permanently lost from the beam either by diffuse reradiation or by transfer through collisions of the second kind. The possibility arises, however, that molecules in the upper quantum state may return to the lower quantum state in such a way as to reinforce the primary beam by "negative absorption." This question will be considered more fully in a later section and it will be pointed out that for absorption experiments as usually performed the amount of "negative absorption" can be neglected.

For the experimental determination of the probability P_{12} in accordance with Eq. (6), we need a knowledge of the integral $\int a d\nu$. This can of course be most successfully obtained from an actual graphical integration under the experimental curve for the absorption coefficient. In the absence, however, of complete enough data for such graphical integration we may sometimes obtain an approximation by putting the integral $\int a d\nu$ proportional to the product of the maximum value a_m and the spectral width $\Delta\nu$ at which the value of a has sunk to one half its maximum value, in accordance with what may best be regarded as an empirical equation.

$$\int_0^\infty a d\nu = K a_m \Delta\nu. \quad (7)$$

If the Drude theory of absorption were correct, it has been shown by Füchtbauer,¹ changing to our notation, that the constant K would have the value $\pi/2$. It has been shown, however, by Bartels³ that the value

⁶ The quantities occurring in articles of Füchtbauer and his associates can be translated to ours with the help of the following equations: $i = I_\nu$; $n\chi = a\lambda/4\pi$; $P = P_{12}$, $\nu' = 2\pi\Delta\nu$; $nk = a\lambda/4\pi$; $b = \Delta\nu$.

$(\pi/2)a_m\Delta\nu$ is 36 per cent too large for the caesium line λ 3612, while the work of Füchtbauer and Hoffman³ on λ 3877 under conditions to produce four times the broadening gave a value 38 per cent too large. Although this shows that the value $\pi/2$ may be seriously in error, it nevertheless indicates that for lines of similar origin, it will often be allowable to assume that K has the same value for the different lines. We can then calculate the ratio of the values of P_{12} for two different lines with the help of the equation

$$\frac{P_{12}}{P'_{12}} = \frac{N_1' h \nu'}{N_1 h \nu} \frac{\int_0^\infty \alpha d\nu}{\int_0^\infty \alpha' d\nu'} = \frac{N_1' \nu'}{N_1 \nu} \frac{a_m \Delta\nu}{a_m' \Delta\nu'} = \frac{N_1' \lambda}{N_1 \lambda'} \frac{a_m \Delta\nu}{a_m' \Delta\nu'}. \quad (8)$$

V. RELATION OF P_{12} , B_{12} , B_{21} , A_{21} AND τ

The quantity P_{12} is the chance per unit time that a molecule will be activated by a beam of light of unit intensity I_ν , intensity being measured in units of energy per unit time, per unit cross section, per unit frequency range. If now the velocity of the light energy is c , it is evident that light of unit intensity would have the density $1/c$, where density u_ν is measured in units of energy, per unit volume, per unit frequency range.⁷ Hence, if we denote by B_{12} the chance of activation per unit time under the action of light of unit density we obviously have

$$B_{12} = c P_{12}. \quad (9)$$

In order to show the relation between the quantity B_{12} first introduced by Einstein and his further quantities B_{21} and A_{21} , we shall next have to present a summary of his method of deriving the Planck radiation law.

Consider a molecule capable of existing in two quantum states with the energy contents ϵ_1 and ϵ_2 , $\epsilon_2 > \epsilon_1$, in equilibrium with black body radiation. For the number of molecules passing in unit time from state 1 to state 2 through the absorption of a quantum of energy, we have

$$-(dN_1/dt) = N_1 u_\nu B_{12} \quad (10)$$

where N_1 is the number of molecules in state 1. For the number passing in the reverse direction we have

$$-(dN_2/dt) = N_2 A_{21} + N_2 u_\nu B_{21} \quad (11)$$

where N_2 is the number of molecules in state 2, A_{21} is the proportionality factor for spontaneous emission, and B_{21} the proportionality factor for emission through negative absorption, this latter process being introduced to preserve the analogy with the classical treatment.

⁷ The velocity with which the *energy* is passing through the absorbing medium is taken as c , the same as the velocity of light in free space. See Sommerfeld, *Phys. Zeits.* **8**, 841 (1907)

If now at equilibrium the number of molecules going in unit time from state 1 to state 2 is equal to the number going in the reverse direction,⁸ we have

$$N_1 u_\nu B_{12} - N_2 u_\nu B_{21} - N_2 A_{21} = 0. \quad (12)$$

In accordance with the Boltzman principle, and the Bohr relation between energy and frequency, however, we may write

$$\frac{N_1}{N_2} = \frac{p_1}{p_2} e^{(\epsilon_2 - \epsilon_1)/kT} = \frac{p_1}{p_2} e^{h\nu/kT} \quad (13)$$

where p_1 and p_2 are the a priori probabilities for states 1 and 2 and ν is the frequency of the absorption line accompanying the passage from state 1 to 2.

Substituting (13) in (12) and solving for u_ν , we obtain

$$u_\nu = \frac{A_{21}/B_{21}}{(p_1/p_2) (B_{12}/B_{21}) e^{h\nu/kT} - 1} \quad (14)$$

Since u_ν must increase to infinity when T is infinite, it is evident that we must have the relation

$$(p_1/p_2) (B_{12}/B_{21}) = 1; \quad B_{21} = (p_1/p_2) B_{12} \quad (15)$$

so that equation (14) may be rewritten in the form

$$u_\nu = \frac{A_{21}}{B_{21}} \frac{1}{e^{h\nu/kT} - 1} \quad (16)$$

Furthermore in accordance with the Wien displacement law we have

$$u_\nu = \text{constant} \times \nu^3 \phi(\nu/T)$$

so that equation (16) becomes

$$u_\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \quad (17)$$

where $8\pi h/c^3$ may be regarded as the empirically determined constant.

This completes Einstein's deduction of the Planck radiation law. We have reproduced it here in order to obtain the relation between B_{12} and A_{21} . By comparison of Eq. (16) and (17) we see that

$$A_{21}/B_{21} = 8\pi h \nu^3 / c^3$$

and by introduction of (15)

$$A_{21} = \frac{8\pi h \nu^3}{c^3} \frac{p_1}{p_2} B_{12} = \frac{8\pi h}{\lambda^3} \frac{p_1}{p_2} B_{12}. \quad (18)$$

⁸ This assumption should be recognized as a distinct postulate and might be called the principle of *microscopic* reversibility. In the case of a system in thermodynamic equilibrium, the principle would require not only that the total number of molecules leaving a given quantum state in unit time shall equal the number arriving in that state in unit time, but also that the number leaving by any one particular path, shall be equal to the number arriving by the reverse of that particular path.

Since we have already shown the possibility of calculating B_{12} from absorption data we can now obtain values of A_{21} from the above equation or indeed by substituting Eq. (6) and (9) in (18) can obtain the following formula for the direct calculation of values of A_{21}

$$A_{21} = \frac{8\pi\nu^2}{c^2 N_1} \frac{p_1}{p_2} \int_0^\infty a d\nu. \quad (18a)$$

The quantity A_{21} , however, as will be seen from Eq. (11), is the specific reaction rate for the monomolecular decay of molecules in state 2 in the absence of radiation. As is well known, the average life τ for molecules undergoing a monomolecular change can easily be shown equal to the reciprocal of the specific reaction rate, and we obtain

$$\tau = 1/A_{21} \quad (19)$$

This completes the derivation of a method of calculating the mean life of molecules in an activated state from data on the intensity of absorption lines. In case the molecules can jump from state 2 to more than one lower state, it is obvious of course that the mean life will be the reciprocal of the sum of the specific reaction rates for the different paths.

VI. THE REINFORCEMENT OF THE PRIMARY BEAM BY NEGATIVE ABSORPTION

We have already called attention to the fact that our analysis of the nature of the absorption coefficient in an ordinary absorption experiment was based on the assumption that all the light absorbed by the quantum jump from state 1 to state 2 was permanently lost from the primary beam either by diffuse reradiation or by collisions of the second kind. The process of negative absorption, however, from analogy with classical mechanics, would presumably be of such a nature as to reinforce the primary beam, and we must assure ourselves that the magnitude of this reinforcement is negligible. This can easily be done.

It is evident from the discussion of the preceding section that the positive and negative absorptions will stand in the ratio

$$N_1 B_{12} / N_2 B_{21} = N_1 p_2 / N_2 p_1$$

It can be shown, however, for the quantum states usually investigated, that N_1 is large compared with N_2 even when allowance is made for the molecules changed up into the higher quantum state by the light used for the experiment; p_2 and p_1 , moreover, are of the same order of magnitude. Hence the reinforcement of the beam by negative absorption is negligible, as originally tacitly assumed.

VII. VALUES OF P_{12} CALCULATED FROM EXPERIMENTAL DATA

We may now proceed to the calculation of values for P_{12} for a number of cases where data are available. The values obtained are collected in

the fourth column of Table I. We give below sufficient data for the repetition of the calculations. Sources of the data are indicated by the initial letters of the authors' names already referred to,^{1,3,4} which are inserted in brackets at the end of the data for a given spectral line.

A. DATA

(in C. G. S. units unless otherwise specified).

Mercury, $\lambda = 2537$ A, $N_1 = 3.33 \times 10^{13}$, $(\lambda/4\pi) \int a d\nu = 5 \times 10^4$ (F. J. and D.)

Caesium, $\lambda = 3877$ A, $N_1 = 4.38 \times 10^{15}$, $(\lambda/4\pi) \int a d\nu = 5.64 \times 10^5$.

For use below, $\lambda a_m/4\pi = 3.74 \times 10^{-7}$, $2\pi\Delta\nu = 84.36 \times 10^{11}$. (F.)

$\lambda = 4593$ A, $N_1 = 8.49 \times 10^{13}$, $\lambda a_m/4\pi = 3.90 \times 10^{-7}$,

$2\pi\Delta\nu = 3.92 \times 10^{11}$. (F.)

$\lambda = 4555$ A, λa_m (for $\lambda 4555$) $= 3.05 \lambda a_m$ (for $\lambda 4593$) under same conditions; and when corrected to same conditions $2\pi\Delta\nu = 4 \times 10^{11}$ for $\lambda 4555$ and $2\pi\Delta\nu = 3.85 \times 10^{11}$ for $\lambda 4593$ (F. and H.)

$\lambda = 3612$ A, P_{12} (for $\lambda 3612$) $= (1/3.69) \times P_{12}$ (for $\lambda 3877$). (B.)

$\lambda = 3617$ A, $\lambda a_m/4\pi = 2.33 \times 10^{-8}$, $2\pi\Delta\nu = 2.35 \times 10^{12}$; under the same conditions $\lambda a_m/4\pi = 11.65 \times 10^{-8}$, $2\pi\Delta\nu = 2.35 \times 10^{12}$ for $\lambda 3612$. (B.)

Sodium, $\lambda = 5890$ A, $N_1 = 2.22 \times 10^{12}$, $\lambda a_m/4\pi = 4.24 \times 10^{-7}$,

$2\pi\Delta\nu = 3.46 \times 10^{11}$. (F.)

$\lambda = 5896$ A, $\lambda a_m/4\pi = 2.09 \times 10^{-7}$, $2\pi\Delta\nu = 3.68 \times 10^{11}$, under same conditions as for $\lambda 5890$. (F. and H.)

Iodine, $\lambda = 5461$ A, $N_1 = 3 \times 10^{10}$, $\lambda a_m/4\pi = 3.5 \times 10^{-7}$,

$2\pi\Delta\nu = 0.6 \times 10^{11}$. (F.)

Hydrogen chloride,* pressure 1 atm., temperature about 20° C. (I.)

| No. of line | λ | a_m | $\Delta\nu$ |
|-------------|------------------------|---------|------------------------|
| 12 | 3.239×10^{-4} | 0.01265 | 1.953×10^{11} |
| 8 | 3.299 | 0.0970 | 1.178 |
| 3 | 3.394 | 0.2200 | 1.334 |
| 2 | 3.415 | 0.2265 | 0.879 |
| 1 | 3.439 | 0.1951 | 1.300 |
| -1 | 3.489 | 0.2040 | 1.474 |
| -2 | 3.516 | 0.3335 | 1.037 |
| -3 | 3.544 | 0.3067 | 1.018 |
| -8 | 3.699 | 0.09545 | 1.311 |
| -12 | 3.846 | 0.01161 | 1.455 |

* The temperature of the gases in Imes' experiments is taken as 20° C for purposes of calculation, since the internal evidence of the article indicates that the work was done with the gases approximately at room temperature. The partial pressure p_{HF} of hydrogen fluoride HF , is unknown for two reasons. In the first place the total pressure of the gas is not stated although it was presumably in the neighborhood of one atmosphere, and in the second place hydrogen fluoride is known to be an associated gas at atmospheric pressure and room temperature. For this reason the results for hydrogen fluoride given in Table I all contain the unknown factor p_{HF} , but have of course perfectly good relative significance. Since p_{HF} is almost certainly less than 1 atm., it is evident that the values of P_{12} , B_{12} and A_{21} for hydrogen fluoride are greater than corresponding values for hydrogen chloride.

TABLE I[§]

(Quantities in C. G. S. units unless otherwise indicated)

| Substance | Line | λ | P_{12} | B_{12} | p_1/p_2 | A_{21} | τ |
|-----------|---|--|--|---|---|---|--|
| Mercury | $n, j, k \rightarrow n', j', k'$ 6, 1, 1 \rightarrow 2, 2, 2 | 2537 Å | 9.60 (10) ⁷ | 2.88 (10) ¹⁸ | 1/3 | 9.68 (10) ⁶ | 1.03 (10) ⁻⁷ |
| Sodium | 3, 1 $\frac{1}{2}$, 1 \rightarrow 3, 2 $\frac{1}{2}$, 2 3, 1 $\frac{1}{2}$, 1 \rightarrow 3, 1 $\frac{1}{2}$, 2 | 5890 5896 | 7.74 (10) ⁸ 4.06 (10) ⁸ | 2.32 (10) ¹⁹ 1.22 (10) ¹⁹ | 1/3 1/3 | 6.21 (10) ⁶ 3.25 (10) ⁶ | 1.61 (10) ⁻⁷ 3.08 (10) ⁻⁷ |
| Caesium | 6, 1 $\frac{1}{2}$, 1 \rightarrow 7, 2 $\frac{1}{2}$, 2 6, 1 $\frac{1}{2}$, 1 \rightarrow 7, 2 $\frac{1}{2}$, 2 6, 1 $\frac{1}{2}$, 1 \rightarrow 8, 2 $\frac{1}{2}$, 2 6, 1 $\frac{1}{2}$, 1 \rightarrow 9, 2 $\frac{1}{2}$, 2 6, 1 $\frac{1}{2}$, 1 \rightarrow 9, 1 $\frac{1}{2}$, 2 | 4555 4593 3877 3612 3617 | 6.67 (10) ⁷ 2.11 (10) ⁷ 8.44 (10) ⁶ 2.29 (10) ⁶ 4.56 (10) ⁶ | 2.00 (10) ¹⁸ 6.33 (10) ¹⁷ 2.53 (10) ¹⁷ 6.86 (10) ¹⁶ 1.37 (10) ¹⁶ | 1/3 1/3 1/3 1/3 1/3 | 1.16 (10) ⁶ 3.56 (10) ⁵ 2.37 (10) ⁵ 7.98 (10) ⁴ 1.58 (10) ⁴ | 8.64 (10) ⁻⁷ 2.80 (10) ⁻⁷ 4.21 (10) ⁻⁶ 1.26 (10) ⁻⁶ 6.33 (10) ⁻⁶ |
| Iodine | — | 5461 | 1.12 (10) ⁴ | 3.36 (10) ¹⁴ | — | 3.40 (10) ² | 2.94 (10) ⁻³ |
| HCl | $m, n \rightarrow m', n'$ 12, 0 \rightarrow 13, 1 8, 0 \rightarrow 9, 1 3, 0 \rightarrow 4, 1 2, 0 \rightarrow 3, 1 1, 0 \rightarrow 2, 1 1, 0 \rightarrow 0, 1 2, 0 \rightarrow 1, 1 3 0 \rightarrow 2, 1 8, 0 \rightarrow 7, 1 12, 0 \rightarrow 11, 1 23/2, 0 \rightarrow 25/2, 1 15/2, 0 \rightarrow 17/2, 1 5/2, 0 \rightarrow 7/2, 1 3/2, 0 \rightarrow 5/2, 1 1/2, 0 \rightarrow 3/2, 1 3/2, 0 \rightarrow 1/2, 1 5/2, 0 \rightarrow 3/2, 1 7/2, 0 \rightarrow 5/2, 1 17/2, 0 \rightarrow 15/2, 1 25/2, 0 \rightarrow 23/2, 1 6, 0 \rightarrow 7, 1 2, 0 \rightarrow 3, 1 1, 0 \rightarrow 2, 1 2, 0 \rightarrow 1, 1 5, 0 \rightarrow 4, 1 11/2, 0 \rightarrow 13/2, 1 3/2, 0 \rightarrow 5/2, 1 1/2, 0 \rightarrow 3/2, 1 5/2, 0 \rightarrow 3/2, 1 11/2, 0 \rightarrow 9/2, 1 | 3.239 μ 3.299 3.394 3.415 3.439 3.489 3.516 3.544 3.699 3.846 3.239 3.299 3.394 3.415 3.439 3.489 3.516 3.544 3.699 3.846 2.395 2.475 2.499 2.578 2.671 2.395 2.475 2.499 2.578 2.671 | 43.0 (10) ⁴ 4.65 " 1.85 " 1.46 " 3.20 " 3.85 " 2.61 " 2.05 " 5.72 " 34.9 " 23.3 " 3.11 " 1.60 " 1.33 " 3.08 " 2.05 " 1.96 " 1.83 " 7.82 " 61.1 " 6.65 (10) ⁴ * 3.77 " 3.04 " 2.35 " 4.04 " 3.69 " 3.17 " 2.82 " 1.97 " 5.77 " | 129 (10) ¹⁴ 14.0 " 5.55 " 4.38 " 9.60 " 11.6 " 7.83 " 6.15 " 17.2 " 105. " 69.9 " 9.33 " 4.80 " 3.99 " 9.24 " 6.15 " 5.88 " 5.49 " 23.5 " 183. " 20.0 (10) ¹⁴ * 11.3 " 9.12 " 7.05 " 12.1 " 11.1 " 9.51 " 8.46 " 5.91 " 17.3 " | 12/13 8/9 3/4 2/3 1/2 $\left\{ \begin{array}{c} \infty \\ 1 \\ 0 \end{array} \right\}$ 2 3/2 8/7 12/11 12/13 8/9 3/4 2/3 1/2 2 3/2 4/3 9/8 13/12 6/7 2/3 1/2 2 5/4 6/7 2/3 1/2 3/2 6/5 | 57.7 5.69 1.75 1.21 1.94 4.48 5.93 3.41 6.38 33.1 31.3 3.80 1.52 1.10 1.87 4.77 3.34 2.71 8.58 57.5 20.5* 8.19 4.81 13.6 13.1 11.4 6.88 4.46 8.52 17.9 | 0.0174 0.176 0.571 0.829 0.515 0.223 0.169 0.293 0.157 0.0303 0.0320 0.263 0.660 0.910 0.535 0.210 0.299 0.369 0.117 0.0174 0.0488† 0.122 0.208 0.0738 0.0764 0.0880 0.145 0.224 0.117 0.0557 |

§ In the abstract of this article which appeared in the Proc. Nat. Acad. 10, 85 (1924) the values of A_{21} and τ for the members of the sodium and caesium doublets were inadvertently interchanged.

* These should be divided by the partial pressure of unassociated fluoride, p_{HF} .

† These should be multiplied by the partial pressure of unassociated fluoride, p_{HF} .

For line No. 1, $\int a d\nu = 4.572 \times 10^{10}$.

The moment of inertia of the molecule⁹ is $J = 2.59 \times 10^{-40}$.

Hydrogen fluoride,* pressure p_{HF} atm. temperature about 20° C. (I.)

| No. of line | λ | a_m | $\Delta\nu$ |
|-------------|------------------------|--------|------------------------|
| 6 | 2.395×10^{-4} | 0.0540 | 4.357×10^{11} |
| 2 | 2.475 | 0.1470 | 3.875 |
| 1 | 2.499 | 0.1470 | 4.203 |
| -2 | 2.578 | 0.1815 | 1.880 |
| -5 | 2.671 | 0.0629 | 5.250 |

The moment of inertia of the molecule⁹ is $J = 1.325 \times 10^{-40}$.

B. METHOD OF CALCULATION AND RELIABILITY OF RESULTS

The value of P_{12} for mercury λ 2537 is probably the most reliable of any of those obtained. The value of N_1 is based on the known vapor pressure of mercury. The value of $\int a d\nu$ is based on experiments in which the width of the line was artificially increased by the presence of hydrogen, nitrogen, argon, or carbon dioxide at various pressures. Graphical integrations were performed with the data obtained at each pressure, and the final figure for $\int a d\nu$ was obtained by extrapolation to zero pressure (F. J. and D.). The value of P_{12} was calculated with the help of Eq. (6) and is quite possibly correct for mercury vapor at zero pressure to within 10 per cent.

The value of P_{12} for caesium λ 3877 is somewhat less satisfactory. The value of N_1 is again based on known vapor pressures, but the value of $\int a d\nu$ comes from one graphical integration with data obtained in a single experiment with added nitrogen at 30 atmospheres pressure (F). Extrapolation to zero pressure would lead to a value about one fourth higher if the effect of nitrogen on the caesium line λ 3877 is the same as on the mercury line λ 2537. The final value of P_{12} was calculated with the help of Eq. (6).

The values of P_{12} for the other caesium lines and the two sodium lines, were calculated either directly or indirectly from the value for caesium λ 3877, with the help of Eq. (8) which assumes the same proportionality between $\int a d\nu$ and $a_m \Delta\nu$ for the different lines. This assumption is not serious compared with other uncertainties. Some of the values are in error owing to the wide extrapolation of vapor pressure necessary to get a value for N_1 . (In making the calculations for all the caesium and sodium lines, Füchtbauer's values of N_1 cited above were decreased by 2.2 per cent, since he based them on an incorrect value of the Loschmidt number).

⁹ Kratzer, *Zeits. f. Phys.* **3**, 289 (1920)

The value of P_{12} for iodine λ 5461 is approximate. It is calculated from Eqs. (6) and (7) assuming $K = \pi/2$.

In all the above calculations it was assumed that the number of molecules per cc in the lowest quantum state N_1 is equal to the total number per cc present. In view of the Maxwell-Boltzmann distribution law this assumption is presumably correct in the case of mercury, caesium, and sodium owing to the high energy levels of the upper quantum states for these atoms.

In the case of the rotation-oscillation spectra of the hydrogen halides, however, the different absorption lines are produced by molecules in different lower quantum states having small differences in energy level and the value of N_1 must be calculated for each of these lower states. These lower states differ from one another only in the number of units of angular momentum of the rotating molecule, that is in the value of the azimuthal quantum number m , the oscillation quantum number n being in every case zero.

Since two variants of the general theory of rotation-oscillation spectra^{9,10} have been developed and complete certainty has not yet been reached as to which is correct, the calculations of P_{12} have been made according to both theories and somewhat different results obtained. According to the first theory, the azimuthal quantum number m , the a priori probabilities p_m , and the number of molecules in the successive quantum states take the values¹¹

$$m = 1, 2, 3, 4, \dots \quad (19)$$

$$p_m = 2m$$

$$N_m = N p_m e^{-m^2 h^2 / 8\pi^2 J k T} \bigg/ \sum_{m=0}^{\infty} p_m e^{-m^2 h^2 / 8\pi^2 J k T} \quad (20)$$

$$= N 2m e^{-m^2 h^2 / 8\pi^2 J k T} (8\pi^2 J k T / h^2) \text{ (approx. at high temperatures)} \quad (21)$$

and according to the second theory the values¹²

$$m = 1/2, 3/2, 5/2, \dots, n-1/2, \dots \quad (22)$$

$$p_m = 2n$$

$$N_m = N p_m e^{-m^2 h^2 / 8\pi^2 J k T} \bigg/ \sum_{m=\frac{1}{2}}^{\infty} p_m e^{-m^2 h^2 / 8\pi^2 J k T} \quad (23)$$

$$= N 2n e^{-(n-\frac{1}{2})^2 h^2 / 8\pi^2 J k T} (8\pi^2 J k T / h^2) \text{ (approx. at high temperatures)} \quad (24)$$

The values of N_1 for the two hydrogen halides were calculated using Eq. (21) and (24). The value of P_{12} for the hydrogen chloride line No. 1, λ 3.439 μ , was calculated direct from Eq. (6) using the value of $\int a d\nu$ given above. This value was determined by performing a graphical integration on a plot of a against ν using the curve given by Imes⁴ in

¹⁰ Kratzer, *Ergebnisse der Exakten Naturwissenschaften*, **1**, 332 (1922)

¹¹ Reiche, *Ann. der Phys.* **58**, 637 (1919). See Case V.

¹² Tolman, *Phys. Rev.*, **22**, 470 (1923)

Fig. 3 as a basis for obtaining values of α and ν . The values of P_{12} for all the other lines for the two halides were calculated with the help of Eq. (8), values of α_m and $\Delta\nu$ being determined from Figs. 3 and 7 in Imes. Imes' data on hydrogen bromide were not employed owing to uncertainty as to the concentration of the bromide which was mixed with an unknown excess of hydrogen.

The values of P_{12} thus calculated for the halides are subject to some uncertainty. Imes' experiments were primarily performed in order to determine the position of the lines rather than intensities of absorption and the reproduction of the absorption curves is on so small a scale as to make their use difficult. Assuming Imes' curves and their reproduction correct, the value of $\int \alpha d\nu$ for line No. 1 is probably correct within 25 per cent. A certain further uncertainty is introduced into the values of P_{12} for the other lines owing to their calculation on the assumption that $\int \alpha d\nu$ is proportional to $\alpha_m \Delta\nu$ instead of determining $\int \alpha d\nu$ by a graphical integration for each line. To test the probable error introduced by this cause, a graphical integration was performed for the hydrogen chloride line No. -8, λ 3.699 μ . The graphical integration gave a value of P_{12} for this line 17 per cent lower than the value reported in Table I. Finally, it should be remembered, of course, that the values of α and ν are for the gases at atmospheric pressure and data for extrapolating to zero pressure are not available. Taking everything into consideration, the values of P_{12} for the hydrogen halides reported in the table are certainly of the right order of magnitude and large differences between the values for different lines undoubtedly correspond to actuality.

All values of P_{12} and dependent quantities are given in Table I to three significant figures, although two figures is perhaps all that the data even for the best cases warrant.

VIII. VALUES OF B_{12} , A_{21} AND τ

Using the values of P_{12} obtained as described above, values of B_{12} , A_{21} and τ have been calculated and are also given in Table I. The values of B_{12} are easily calculated with the help of Eq. (9).

In order to calculate the values of A_{21} , a knowledge of the a priori probabilities of initial and final quantum states is necessary. The second column in Table I gives the quantum numbers corresponding to the initial and final states for the particular line in question. The quantum numbers for mercury, sodium and caesium are assigned on the basis of Bohr's considerations,¹³ n , j , k being respectively the total, inner and azimuthal quantum numbers for the lower quantum state, and n' , j' , k'

¹³ Bohr, Ann. der Phys. **71**, 228 (1923)

for the upper quantum state reached by the absorption. The quantum numbers for the halides are assigned on the basis of the two variant theories already mentioned, m and n being respectively azimuthal and oscillation quantum numbers. The a priori probabilities for the quantum states of mercury¹⁴ were taken as $3(2k-1)$; for sodium and caesium¹⁴ as $2(2k-1)$; for iodine, in the absence of available information, as the same for both quantum states; and for the hydrogen halides as $2m$ on the basis of the first theory¹¹ and as $2(m+\frac{1}{2})$ on the basis of the second theory.¹² (Unity and infinity have also been inserted as possible values for the a priori probability of the state $m=0$, $n_2=1$ which has been so puzzling for the first theory.) Using the ratios p_1/p_2 obtained in the above manner, values for A_{21} have then been calculated with the help of Eq. (18).

The values of τ given in the last column of the table are merely the reciprocals of the corresponding values of A_{21} . In case the molecule can jump from the upper quantum state under consideration to more than one lower quantum state, the value of τ thus obtained is the mean life that the molecules would have if the particular jump considered were the only one possible. To get the actual mean life in such a case for all the molecules in the upper quantum state we should have to take the reciprocal of the sum of the values of A_{21} for all the different jumps possible. For the upper quantum states considered only one jump is possible in the case of mercury and sodium, but more than one is possible in the case of caesium (combination lines) and in the case of most of the hydrogen halide states.

IX. *COMPARISON OF RESULTS WITH OTHER EXPERIMENTAL DATA

It is a matter of great importance to compare the values of A_{21} and τ obtained in these calculations with those obtained by other if possible more direct experimental methods. Unfortunately direct methods of measuring these quantities are by no means easy to find and indeed this is one of the reasons for resorting to the method presented above.

One direct method for the measurement of τ which has been partially successful has been to measure the decay in the luminosity of canal rays whose velocity is known from the Doppler effect. By the use of this method Wien obtained $\tau=2.3 \times 10^{-8}$ sec. for both the β and γ lines of

¹⁴ At the present stage of theoretical development, it is difficult to assign correct a priori probabilities to the quantum levels of mercury, sodium and caesium, but the above assignment is presumably of the right order of magnitude which is sufficient for our present considerations. In making the calculations the above expressions were taken as giving the a priori probability for a given k and any specified j . It is possible, however, that the expressions should really be taken as giving the total a priori probability for a given k and all the j 's going with it (see Bohr, l. c. 13, pp. 276 and 279).

hydrogen, while Dempster obtained $\tau = 5 \times 10^{-8}$ sec. for the β line.¹⁵ Wien also made some measurements by the canal ray method on oxygen and nitrogen lines, but apparently the method is not adapted for most substances, and no data are available for a direct comparison of canal ray results with ours. It is interesting to note, however, that the values of τ for *electronic* jumps obtained by the canal ray method fall in the region covered by our values of τ for roughly similar jumps.

Wood¹⁶ has shown by direct measurements that τ for the mercury line λ 2537 must at least be less than 7×10^{-5} seconds, while Frank and Grottrian¹⁷ by assuming that τ is of the order of 10^{-8} seconds have been able qualitatively to account for certain phosphorescence effects in mercury vapor observed by themselves and Phillips.¹⁸

Foote and Mohler¹⁹ have shown that the value $\tau = 3 \times 10^{-8}$ for the *D* lines of sodium would account for Zahn's results on the energy emitted by a sodium flame, and this is in rough agreement with our value for the same lines.

The above recital practically exhausts previous information as to pertinent values of τ . It is evident however that the meager data available confirm the general correctness of our method of calculation.²⁰

X. QUALITATIVE LAWS GOVERNING THE RATE OF DECAY OF ACTIVATED MOLECULES

In spite of some uncertainty attaching to the results and the somewhat limited material available, it may nevertheless be useful to formulate tentatively some of the laws governing the rate of decay of activated molecules.

a. The mean life of molecules and atoms in upper quantum states may vary for different states at least over the range from 1 to 10^{-8} seconds.

¹⁵ Wien, Ann. der Phys. **60**, 597 (1919); **66**, 229 (1921)

Dempster, Phys. Rev. **15**, 138 (1920). The interpretation of the canal ray results is by no means simple, since it necessitates a consideration both of the rate at which activated molecules are leaving the upper quantum state and the rate at which they then emit energy on their way to the lower quantum state. See Mie, Ann. der Phys. **66**, 237 (1921)

¹⁶ Wood, Proc. Roy. Soc., A **99**, 362 (1921)

¹⁷ Frank and Grottrian, Zeits. f. Phys. **4**, 89 (1921)

¹⁸ Phillips, Proc. Roy. Soc. A **89**, 39 (1914)

¹⁹ Foote and Mohler, "The Origin of Spectra," New York, 1922; pp. 165-169. Foote and Mohler actually used the value $\tau = 10^{-8}$, but their calculations were made on a basis which was tantamount to assuming unity for the ratio of a priori probabilities p_1/p_2 . With the assumption used in the present article as to a priori probabilities their value of τ must be multiplied by 3.

²⁰ Since this article was first written, and the results of the calculations published in the Proc. Nat. Acad. **10**, 85 (1924), the value of τ obtained for the mercury line has been very satisfactorily confirmed by the calculations of Turner based on an entirely different method (see Phys. Rev. **23**, 464, 1924).

b. The rate of decay is not a simple function of the frequency of the emitted light. The rate corresponding to the emission of a line of higher frequency may be greater or less than that for a line of lower frequency.

c. The data now available for the alkali doublets indicate a higher rate of decay the smaller the change in total quantum number for the line under consideration.

d. In the case of the alkali doublets $1s - mp_1$ and $1s - mp_2$ (Paschen-Götze notation) the rate of decay from a given mp_1 state is m times as great as from the corresponding mp_2 state.²¹ (This is merely another way of stating a conclusion already reached by Füchtbauer and Hofmann.³)

e. In the case of the rotation-oscillation spectra of the hydrogen halides, the rate of decay is greater for quantum states with one unit of oscillation and many of rotation, than for those with one unit of oscillation and only a few of rotation.

f. In the case of the spectra of hydrogen chloride and hydrogen fluoride, for the same quantum numbers, the rate of decay is greater for the molecule with the greater frequency of oscillation.

With regard to the first of the qualitative laws stated above, the writer has had the pleasure of discussing the surprisingly low values calculated for the rate of decay of oscillating hydrogen chloride with Professor Paul Ehrenfest. The writer himself is inclined to believe that these slow rates of decay correspond approximately with reality, nevertheless certain other possibilities must be considered. The calculated rates of decay may come out too low either because of the use of too large values for N_1 or too small values for $\int ad\nu$. Since hydrogen chloride is not an associated gas, as is the case for hydrogen fluoride, the values of N_1 employed can not be incorrect for this reason. There is, however, the bare possibility that the hydrogen chloride molecule may have quantum states now unknown to us of low enough energy content so that an appreciable number of molecules are drawn away from the states of rotation for which we have calculated the values of N_1 . As to the values of $\int ad\nu$ which were employed in the calculations, it should be pointed out that they were determined experimentally for hydrogen chloride at one atmosphere pressure and much larger values might be obtained at lower pressures, this would make the calculated chance for the emission of a quantum come out greater for an isolated molecule. The fact that the value for the mercury line λ 2537 is decreased by only fifty per cent when nitrogen at 50 atmospheres pressure is added might not rule out a much larger effect of collisions in the case of quantum jumps so different in nature. The

²¹ It is possible that the difference in the intensities of the members of a doublet can be partly accounted for by a different assignment of a priori probabilities from that used in this article, and partly by an application of the correspondence principle in the way indicated by Sommerfeld and Heisenberg, *Zeits. f. Phys.* **11**, 131 (1922).

matter can of course be settled experimentally by determining $\int a d\nu$ for hydrogen chloride gas at more than a single pressure. Before leaving this matter it should be pointed out that even if the values of A_{21} for oscillating hydrogen chloride molecules are as small as calculated, nevertheless the actual mean life of oscillating molecules is affected by the fact that more than a single downward quantum jump may be possible from the state 2 under consideration, and by the possibility of giving up energy by collisions of the second kind.

XI. RATE OF DECAY AND BOHR CORRESPONDENCE PRINCIPLE

A theoretical method of predicting values of A_{21} would be very important. The Bohr correspondence principle has already proved its value for approximate calculations of the relative intensities of spectral emission lines,²² which are closely related to relative values of A_{21} . The possibility of calculating absolute values of A_{21} at least approximately from the Bohr correspondence principle is an attractive one to consider. The most hopeful method of procedure to try would be to express the electric moment of the emitting molecule by a Fourier analysis, calculate by classical methods the rate of emission of energy due to the particular partial vibration that corresponds to the quantum jump under consideration, and equate this rate of energy emission, which would be ascribed by the classical theory to each individual molecule, to $A_{21}h\nu$ which is the average rate ascribed by the quantum theory to all the emitting molecules. The writer hopes to make this method of calculating values of A_{21} the subject of a later article.

XII. CONCLUSION

Before closing it should be pointed out that the results obtained in this paper are very intimately dependent on the point of view expressed by Einstein² in his 1917 paper, as to the emission and absorption of radiation. If the results thus obtained are always found to be in agreement with those obtained by other methods, it will certainly lend support directly to the Einstein point of view as to the emission and absorption of radiant energy by atoms and molecules, and hence somewhat indirectly to the extreme point of view of the existence of light quanta.

The writer wishes to emphasize the importance of further accurate determinations of values of $\int a d\nu$, and the development of other methods for determining the rate of decay of activated atoms and molecules.

The writer wishes to express his thanks to Mr. James B. Friauf for assisting in the computations involved in the article.

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PASADENA, CALIFORNIA,
January 10, 1924.

²² H. A. Kramers, "Intensities of Spectral Lines," Copenhagen Academy 1919.